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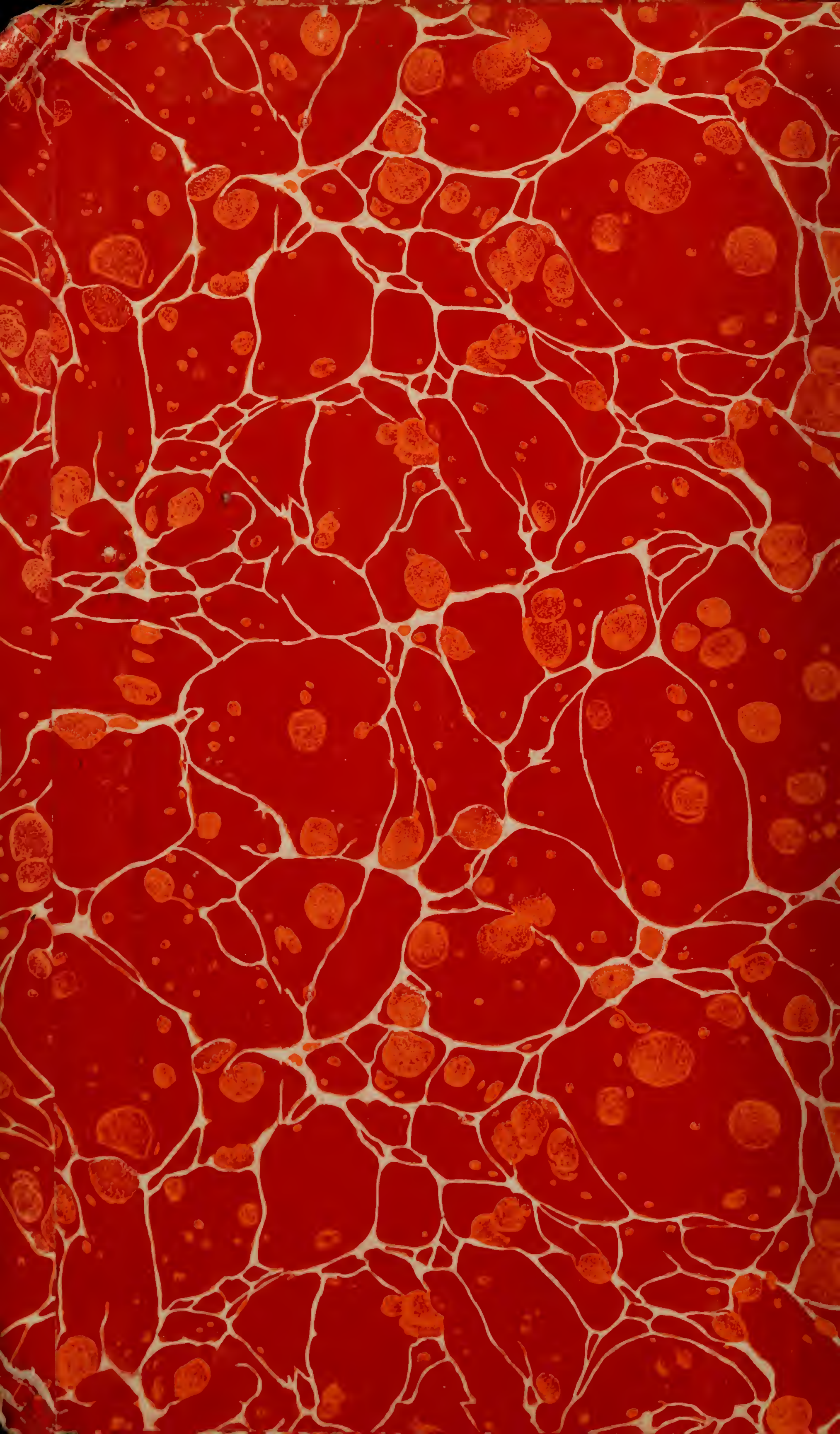

RP514

THE HEAT CAPACITY, HEAT OF SUBLIMATION, AND HEAT OF SOLUTION OF PHOSPHORUS PENTOXIDE

By Mikkel Frandsen

ABSTRACT

The heat capacity of the vapor of P_2O_5 at atmospheric pressure and at temperatures between the sublimation point and 1,100° C. was determined by subliming the P_2O_5 through a silica tube heated in a tubular electric furnace with a nearly constant temperature along the main part of the axis, collecting the vapor in a Dewar flask charged with water, measuring calorimetrically the sum of the heat content of the vapor and the heat of solution, and deducting the latter. The method was tested by similar experiments with superheated steam, and the results were found to be in good agreement with accepted results for this substance. For P_2O_5 vapor, $C_{p\ (1\ \mathrm{atm.})}=36.8\pm1.0$, cal.$_{15}$ mole^{-1} °$C.^{-1}$ over the range 360° to 1,100° C.

The heat capacity of the usual metastable crystalline form of phosphorus pentoxide between room temperature and the sublimation point was determined by the calorimetric method of mixtures applied to samples sealed in silica tubes. Result, $C_p=(22.17+0.07804t-8.45\times10^{-5}t^2)\pm1.6$ per cent, cal.$_{15}$ mole^{-1} °$C.^{-1}$, between 25° and 350° C.

The heat of sublimation was calculated as the difference in heat content of the vapor and the solid, respectively, at the sublimation point, and found to be $L=8.8\pm1.3$ kg–cal.$_{15}$ mole^{-1} at 358° C.

The heat of solution of metastable crystalline phosphorus pentoxide at 25° C. was measured by breaking sealed glass tubes, containing this material, under water in a calorimeter. When metaphosphoric acid is formed, $Q=42.0\pm2.1$ kg–cal.$_{15}$ mole^{-1}, and when orthophosphoric acid is formed $Q=54.4\pm2.1$ kg–cal.$_{15}$ mole^{-1}. The heat of transformation of meta— into orthophosphoric acid was computed to be 6.2 ± 1.9 kg–cal.$_{15}$ mole^{-1}.

The sublimation point was estimated, from various vapor pressure measurements performed by other investigators, to be 358° ± 7° C.

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I. INTRODUCTION

The information which may be obtained from the literature in regard to the thermal properties of phosphorus pentoxide is incomplete and very uncertain. This may probably be ascribed partly to the difficulties experienced in working with this substance at elevated temperatures and partly to the failure of early investigators to obtain the substance in a pure state. Phosphorus pentoxide is extremely hygroscopic, and the phosphoric acid, formed by absorption of moisture, will, at high temperatures, attack nearly all materials from which a suitable apparatus may be constructed. Glass and silica, when heated in contact with an appreciable amount of moist phosphorus pentoxide, invariably break on cooling, apparently on account of differences in shrinkage.

The present paper presents the results of determinations of the heat capacity of metastable crystalline phosphorus pentoxide between room temperature and the sublimation point, the heat of sublimation of this substance, and the heat capacity of the vapor between the sublimation point and 1,100° C. These quantities have never been measured before. The heat of solution of metastable crystalline phosphorus pentoxide in water has been redetermined, and an average value for the sublimation point has been derived from vapor pressure measurements performed by other investigators.

The investigation was undertaken at the request of the Fixed Nitrogen Research Laboratory of the Department of Agriculture in order to supply thermal data needed in a thermodynamic investigation of the industrial processes involved in the manufacture of fertilizer from phosphate rock.

II. PURIFICATION OF MATERIAL

The phosphorus pentoxide used in this investigation was prepared from one of the best grades of the commercial product by sublimation in a current of oxygen in a 2-inch iron tube at about 800° C., according to the method of Finch and Fraser.[1] The iron tube was heated electrically instead of by gas. In this process lower oxides of phosphorus are oxidized completely, as shown by the fact that a solution of the purified product does not reduce solutions of silver nitrate [2] or mercuric chloride.[3]

After sublimation the oxidized product absorbs some moisture from the atmosphere, but by resublimation in the absence of atmospheric moisture and at pressures not exceeding 1 atmosphere, it yields pure crystalline phosphorus pentoxide.

III. HEAT CAPACITY OF PHOSPHORUS PENTOXIDE VAPOR

1. APPARATUS AND PROCEDURE

The method by which the heat capacity of phosphorus pentoxide vapor was determined consisted in subliming phosphorus pentoxide through a silica tube placed in an electric furnace in which the vapor was heated to the desired temperature. Emerging in jet form through a narrow opening the heated vapor was collected in a calorimeter, consisting of a Dewar flask containing a known amount of water, and there dissolved. The heat capacity of the calorimeter, the rise in temperature, and the heat of solution were then used in calculating the heat content of the vapor at the temperature at which it emerged from the furnace.

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[1] Finch, G. I., and Fraser, R. P., J. Chem. Soc., vol. 129, pp. 117–119, 1926.
[2] Finch, G. I., and Peto, R. H. K., J. Chem. Soc., vol. 121, p. 692, 1922.
[3] Whitaker, H., J. Chem. Soc., vol. 127, p. 2219, 1925.

The apparatus used is shown in Figure 1. A Pyrex flask, *F*, contained the purified phosphorus pentoxide mixed with a little phosphoric acid, which had been formed by the action of absorbed moisture. Through a ground joint, *A*, the glass flask was connected to an apparatus made from vitreous silica, which is able to withstand the action of phosphorus pentoxide at high temperatures. Moisture was expelled from the silica apparatus, before the ground joint connection was made, by passing a current of dry air through it while the walls were heated. The subsequent entrance of moisture through the ground joint was prevented by surrounding this with a seal of molten tin covered with a layer of carbon black. A small electric furnace, *E*, maintained a temperature of about 500° C. around the ground joint, whereby the tin was kept molten and condensation of phosphorus pentoxide in this part of the apparatus was prevented. The lower end of the furnace was plugged with asbestos to prevent draft around the heated connection. Pure phosphorus pentoxide was first sublimed from *F* into the silica bulb, *C*, where it condensed in the usual metastable, crystalline form. Care was taken not to heat the flask *F* too strongly in order to avoid volatilization of metaphosphoric acid from the mixture. Even after sublimation it was necessary to keep the flask *F* heated, for two reasons: First, the flask invariably broke on cooling, owing to different rates of contraction of the glass and the residue; second, the phosphorus pentoxide subsequently sublimed out of *C* was thereby prevented from returning to the flask *F*.

The silica tube, *B*, has at the center a well in which a platinum-platinumrhodium (10 per cent Rh) thermocouple was placed. From the lower end of the well four amply spaced projections extend close to the walls of the tube; they served to protect the well from being broken off by its own weight when the apparatus was in a horizontal position. The end of the silica tube, *B*, is drawn out into a narrow spout, 3 mm in diameter at the orifice, and is connected by another ground joint to the silica tube, *M*, and to a drying tube that served to guard the inside of the apparatus against atmospheric moisture.

The main furnace, *G*, contained two mutually independent heating coils, by means of which a nearly uniform temperature could be maintained throughout the main part of the furnace, anywhere in the interval from room temperature to 1,100° C. This is illustrated in Figure 2, which shows the temperatures that were maintained along the axis of the furnace in five sets of determinations made both on phosphorus pentoxide and on water. Temperatures below the thermocouple well were measured with thermocouples inserted through the bottom of the furnace. In each case the external resistances were adjusted until the temperature at the bottom of the well was equal to that at a distance of 40.6 cm from the top of the furnace. The temperature at these two points will hereafter be designated as the furnace temperature. By reproducing the temperatures at those two points the temperatures prevailing in various other parts of the furnace during any run could be reproduced automatically as often as desired. Figure 2 represents conditions in the furnace before the vapor passed into it. The dotted portion added to the middle curve helps to show the effect of the auxiliary heater, as it represents temperatures observed in the lower half of the furnace when the auxiliary heater remained turned off.

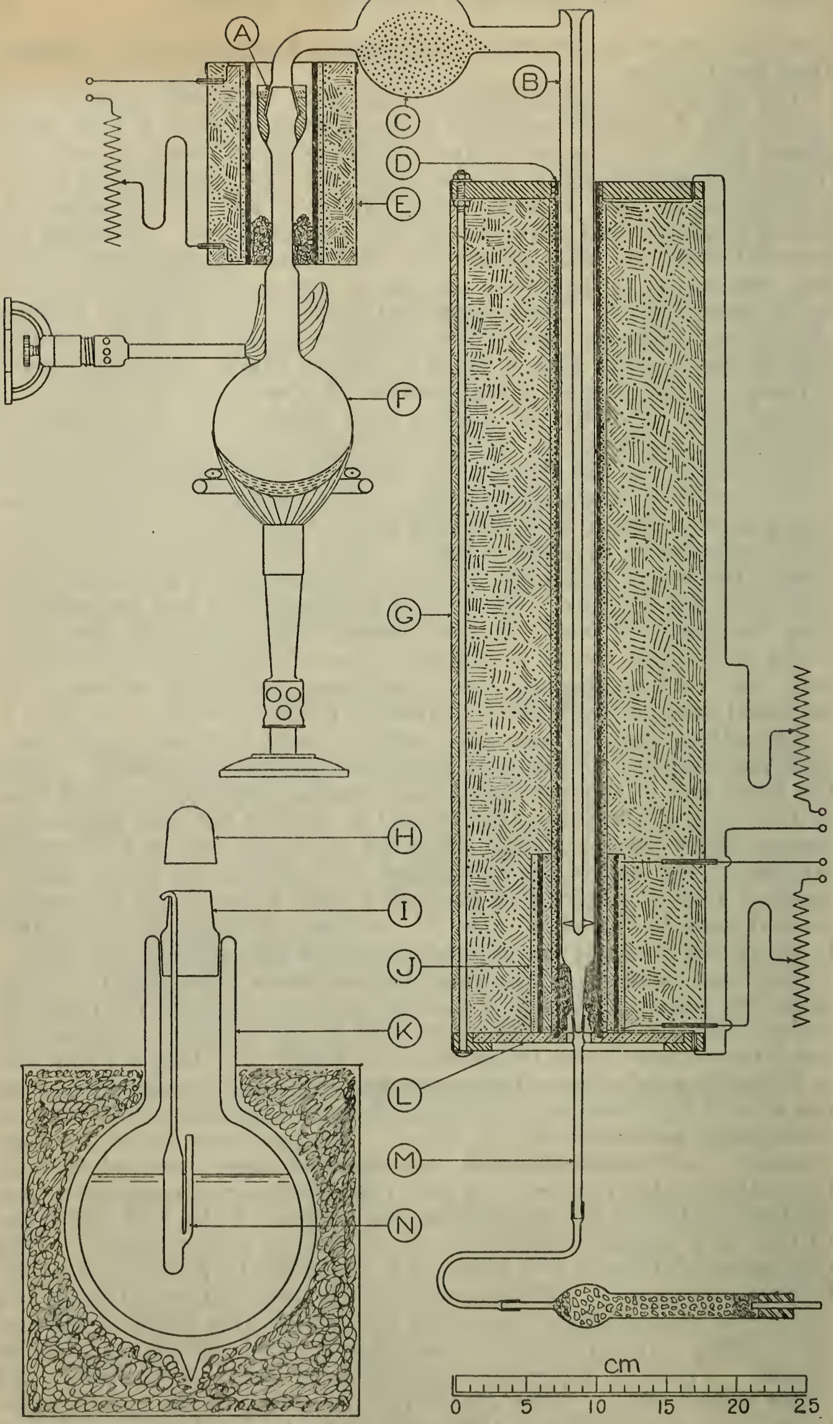

FIGURE 1.—*Apparatus for determining the heat content of vapor of phosphorus pentoxide*

The 2-liter Dewar flask, *K*, shown in Figure 1, served as a calorimeter and was charged with 1,500 g of distilled water in preparation for a run. It could be closed with a cap, *H*, and a collar, *I*, both of which were made from Pyrex laboratory glass and ground to fit. The piece, *N*, suspended from a small notch in the collar, served during a run as an outlet for air and as a trap for water vapor and phosphorus pentoxide; it was placed in position after the fore period, just before the heated vapor was passed into the calorimeter, and was pushed over the edge of the collar into the flask just after, so that the cap might be put on and the flask shaken. The neck and top parts of the flask were covered with a couple of large cloths. The calorimeter was stirred by shaking, and a Beckmann thermometer was used for measuring the temperature rise. The calorimeter was kept in a room with practically constant temperature, except during the short period in which hot vapor was charged into it.

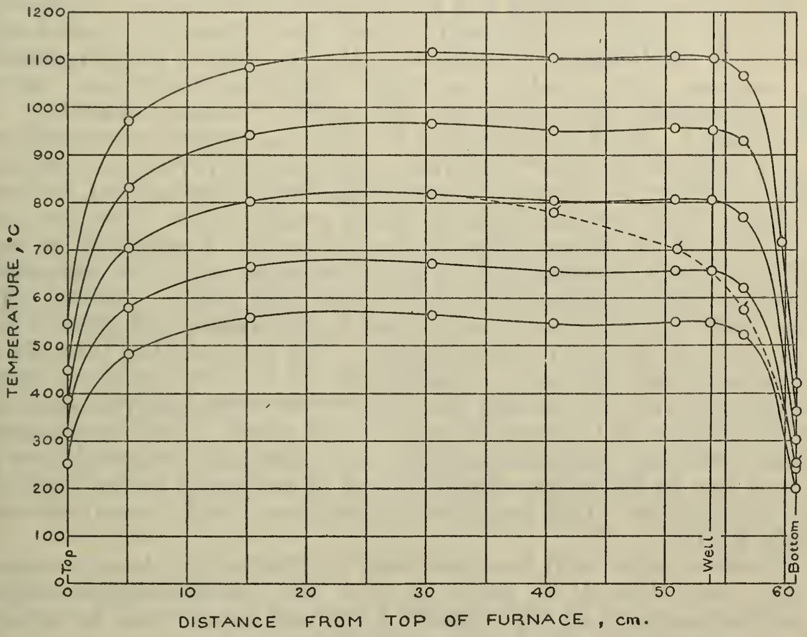

FIGURE 2.—*Temperatures along the axis of the furnace*

In preparing for a run the furnace, *G*, was brought to the desired temperature, the calorimetric fore period was recorded and the Dewar flask with its contents was weighed. The tube, *M*, was then removed, and phosphorus pentoxide was sublimed through the furnace by heating the bulb, *C*, with one or two gas burners. The upper part of the silica tube, *B*, must also be heated to prevent condensation in it, and when a high temperature was desired the vapor could be preheated considerably in that part of the tube before entering the furnace. In two to three minutes the issuing vapor had heated the constricted outlet sufficiently, and the calorimeter, with the cap removed, the air-outlet piece, *N*, in position, and the water in a swirling motion, was brought under the spout and the collar, *I*, pressed against the alundum plate, *L*. At the higher temperatures most of the vapor reached the water and dissolved; at lower temperatures it condensed, to a considerable extent, in the neck of the Dewar flask. The calorimeter was held under the spout for a measured length of time, usually 90 seconds, during which period 4 to 16 g of phosphorus pentoxide was partly condensed and partly dissolved in it. The calorimeter was then removed from the furnace and shaken, after replacement of the cap, until the phosphorus pentoxide was completely dissolved and the neck cooled off to the temperature of the solution; this usually required about 10 minutes. Subsequently, the Dewar flask with contents was weighed, and the after period recorded.

2. SUPPLEMENTARY DETERMINATIONS

In connection with each experiment various supplementary determinations and corrections had to be made before the heat content of the vapor could be calculated. Thus, the amount of phosphorus pentoxide condensed and dissolved in the calorimeter was determined by analysis of the resulting solution. The true temperature rise in the calorimeter was found by the graphic method described by Dickinson.[4] Blank experiments, in which no phosphorus pentoxide was sublimed through the furnace, provided a correction for heat taken up from the furnace through radiation and conduction, for heat exchange with the surroundings during weighing, etc. The increase in weight of the Dewar flask during the period of condensation and solution equals the weight of the phosphorus pentoxide less the weight of water evaporated out of the flask during that period. Accordingly, this small amount of water was found by difference, and a correction was made for its heat of vaporization. The inner shell of the neck of the calorimeter was heated considerably by the hot vapor and must be cooled slowly by shaking the water upon it gradually in order to avoid cracking of the glass or evolution of steam. In the meantime, some of the heat was transmitted to the outer shell, whence a part of it was lost to the surroundings instead of returning to the inside of the calorimeter. This heat loss was estimated and corrections were made for it.

However, there still remained two supplementary determinations which were difficult to make in runs with phosphorus pentoxide. The thermocouple at the bottom of the well would tend to register the temperature of the walls instead of that of the vapor; moreover, the vapor suffered a certain drop in temperature, dependent upon the rate of flow, in passing from the level of the thermocouple to the orifice of the spout. Measurements of the temperature of the vapor at the orifice of the spout were therefore desirable. Again, the radiation from the furnace to the calorimeter was greater in the main experiments than in the blank experiments, because in the former the spout had been heated by the first, uncollected vapors. It follows that the temperature of the spout before and during a run ought to be measured in order that a correction for the increase in radiation during a run might be made. These determinations were made in runs with steam, and from the results corresponding data were calculated for phosphorus pentoxide, which in direct measurements is apt to attack the thermocouple and which in general is more difficult and more expensive to work with than steam.

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[4] Dickinson, H. C., B. S. Bull., vol. 11, p. 231, 1915.

3. TEST OF THE METHOD WITH STEAM

As the heat capacity of steam at high temperatures is relatively well known, experiments on steam make it possible to estimate the accuracy with which determinations with this apparatus can be made. A series of experiments and appertaining supplementary determinations were accordingly made on water vapor. The main series of experiments with steam consisted of two or three runs at each of five different temperatures in the range from 500° to 1,100° C.

(a) PROCEDURE

In the steam experiments the calorimeter was held under the spout for the same length of time as in the phosphorus pentoxide runs, and the rate of vaporization was so chosen that the amount of heat transferred to the calorimeter became roughly the same as in the phosphorus pentoxide runs, usually corresponding to a temperature rise of from 3° to 5° C. in the calorimeter.

The amount of steam condensed in the calorimeter was found as the increase in weight of the Dewar flask with contents. In contrast to phosphorus pentoxide, which was completely condensed in the calorimeter, an appreciable amount of steam left the Dewar flask again without condensing. The weight of this uncondensed steam and the temperature at which it left the Dewar flask had to be ascertained in order that a correction might be made for the amount of heat thus escaping the calorimeter. To this end supplementary experiments were performed with the same rate of vaporization as in the main experiments. The rate of vaporization from the flask, F, was found by determining its loss in weight in about half an hour, during which period the amount condensed in the calorimeter was determined twice in the same manner as during the main experiments. The weight of steam escaping condensation during the experimental period was then easily found by difference. Fortunately, it was not necessary to know the exit temperature of the uncondensed steam very accurately because the amount of the escaping steam was relatively small. From several observations its temperature was estimated to be about 110° C.

The superheated vapor entered the calorimeter, not at the furnace temperature, but at the temperature which it had at the orifice of the spout. This temperature was measured with three platinum-platinumrhodium (10 per cent Rh) thermocouples the wire diameters of which were 0.644, 0.405, and 0.202 mm, respectively. These thermocouples were successively placed at the center of the orifice with at least 50 mm of the wires adjoining the weld set in vertical position in order to have them surrounded and heated by the issuing jet of vapor. With each couple, measurements were made before and during vaporization. The correct temperatures were subsequently obtained by plotting the observed temperatures against the cross-sectional area of the wires, and extrapolating back to the axis at which this area becomes zero.

The temperatures at the level of the well bottom were found to be identical inside and around the well, both before and during vaporization. These temperatures were not changed by the passage of vapor through the silica tube; at least, they remained constant during the usual preheating period of 3 minutes and the subsequent calorimetric period of 90 seconds. It took from 2 to 3 minutes for the vapor to heat the spout, during which period the temperatures at the upper end of the spout and at the orifice increased and became constant. In the steady state thus established the temperature of the vapor at the upper end of the spout was equal to, or only about one degree lower than, the furnace temperature. From this it may be seen that the vapor actually was heated to the furnace temperature; that is, to the temperature at the bottom of the well, which was a little lower than the temperature in the middle of the furnace, as may be seen from Figure 2. In the steady state the temperature of the vapor at the orifice was appreciably lower than the furnace temperature; for example, it was found to be 3° and 36° C. below the furnace temperature at 550° and 1,100° C., respectively, at the usual rate of vaporization.

The temperature of the spout itself was also measured, both before and after the preheating period, in order that a correction might be made for the increased radiation from the heated spout, which escaped measurement in the blank experiments.

(b) DATA AND DISCUSSION

The main series of experiments with steam consisted in 12 runs, details of which are given in Table 1. The furnace temperatures employed in these experiments were in each case close to one of the five temperatures, 550°, 650°, 800°, 950°, and 1,100° C., which also were approximated in the experiments with phosphorus pentoxide. The difference between the furnace temperature and the temperature of the vapor at the orifice is the drop in temperature which the vapor suffered in passing from the bottom of the well to the orifice of the spout. The rate of vaporization was close to 3.8 g of water per minute in all experiments. In runs 4 and 5 the experimental period was 2.0 minutes; in all the other runs it was 1.5 minutes. The experimental period multiplied by the rate of vaporization equals the sum of condensed and uncondensed vapor. The heat loss from the outer shell of the neck of the calorimeter is independent of the furnace temperature. This is due to the fact that in experiments with steam the temperature of the inner shell did not exceed the boiling point of water, on account of reevaporation from the moist inner surface.

TABLE 1.—*Determinations of the heat content of superheated steam*

Run No.	Furnace temperature	Temperature of vapor at orifice	Rate of vaporization	Weight of condensate	Weight of uncondensed vapor	Heat transferred to calorimeter	Correction from blank experiments	Final calorimeter temperature
	°*C.*	°*C.*	*g Min*$^{-1}$	*g (vac.)*	*g (vac.)*	*cal.*$_{15}$	*cal.*$_{15}$	°*C.*
1	546	543	4.115	5.407	0.766	4,829	255	23.86
2	548	545	4.138	5.441	.766	4,940	313	24.37
3	549	546	4.081	5.356	.766	4,915	347	24.94
4	649	644	3.566	6.572	.561	6,174	326	25.60
5	650	645	3.698	6.836	.561	6,398	371	24.70
6	803	795	3.599	5.045	.353	5,111	290	25.98
7	804	796	3.622	5.080	.353	5,191	303	25.63
8	952	934	3.687	5.166	.364	5,927	409	25.61
9	953	935	3.273	4.680	.230	5,083	180	28.77
10	947	929	3.876	5.389	.425	6,193	391	25.83
11	1,105	1,069	4.378	5.674	.893	6,948	332	29.51
12	1,096	1,060	3.503	4.578	.676	5,807	400	28.22

TABLE 1.—*Determinations of the heat content of superheated steam*—Continued

Run No.	Increase of radiation from spout	Heat lost from neck	Correcting to 25° C. (add)	Heat transferred by uncondensed vapor	Total heat content H_t-H_{25}	Sensible heat (obs.) H_t-H_{100}	Sensible heat (calc.) H_t-H_{100}	$\frac{\text{Obs.}-\text{Calc.}}{\text{Obs.}}\times 100$
	cal.$_{15}$	*cal.*$_{15}$	*cal.*$_{15}$	*cal.*$_{15}$	*cal.*$_{15}$ *mole*$^{-1}$	*cal.*$_{15}$ *mole*$^{-1}$	*cal.*$_{15}$ *mole*$^{-1}$	*Per cent*
1	3	50	−6	158	14, 850	3, 781	3, 850	−1. 88
2	3	50	−3	161	14, 933	3, 864	3, 869	−. 13
3	3	50	0	163	14, 973	3, 904	3, 878	. 67
4	7	62	4	145	15, 795	4, 726	4, 775	−1. 04
5	7	62	−2	140	15, 656	4, 587	4, 784	−4. 30
6	10	50	5	114	16, 967	5, 898	6, 187	−4. 90
7	10	50	3	116	17, 078	6, 009	6, 196	−3. 11
8	18	50	3	155	18, 827	7, 758	7, 523	3. 03
9	18	50	18	96	18, 695	7, 626	7, 533	1. 22
10	18	50	4	183	18, 905	7, 836	7, 474	4. 62
11	25	50	26	429	19, 807	8, 738	8, 849	−1. 27
12	25	50	15	336	20, 112	9, 043	8, 760	3. 13

The following notation may be used in calculating the heat content of the vapor at the orifice temperature:

H_t = molal heat content of steam at t° C.
H_{25} = molal heat content of water at 25° C.
Q = amount of heat transferred to the calorimeter.
b = correction obtained by blank experiments.
Δr = increase in radiation from the preheated spout.
Δn = heat lost from the neck of the Dewar flask.
t_f = final calorimeter temperature.
f = correction for deviation of t_f from 25° C.
c = weight of condensed vapor in grams.
u = weight of uncondensed vapor in grams.

We must have

$$H_t-H_{25}=\left[Q-b-\Delta r+\Delta n+f+\frac{u}{18.016}\,(H_{110}-H_{25})\right]\cdot\frac{18.016}{u+c} \qquad (1)$$

and

$$f=(t_f-25)\cdot c \qquad (2)$$

According to the determinations by Osborne, Stimson, and Fiock[5] $H_{100}-H_{25}=2{,}675.99-104.71$, international joules per gram or

$$H_{100}-H_{25}=11{,}069 \text{ cal.}_{15} \text{ mole}^{-1} \qquad (3)$$

Assuming the heat capacity of steam between 100° and 110° C. to be 2.012 international joules per gram per °C.[6], we find

$$H_{110}-H_{100}=86.61 \text{ cal.}_{15} \text{ mole}^{-1} \qquad (4)$$

Addition of equations (3) and (4) gives

$$H_{110}-H_{25}=11{,}156 \text{ cal.}_{15} \text{ mole}^{-1} \qquad (5)$$

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[5] Osborne, N. S., Stimson, H. F., and Fiock, E. F., B. S. Jour. Research, vol. 5 (RP209), p. 479, 1930.
[6] International Critical Tables, vol. 5, p. 82, 1929

From equations (1), (2), and (5) we then obtain

$$H_t - H_{25} = \left[Q - b - \Delta r + \Delta n + (t_f - 25) \cdot c + \frac{u}{18.016} \times 11{,}156 \right] \frac{18.016}{u+c} \quad (6)$$

The heat content of the vapor at the orifice temperature is calculated by substituting in equation (6) the experimentally determined data in Table 1.

The amount of heat, a, transferred to the calorimeter by the uncondensed vapor is

$$a = (H_t - H_{110}) \times \frac{u}{18.016} \quad (7)$$

which with equation (5) gives

$$a = [(H_t - H_{25}) - 11{,}156] \cdot \frac{u}{18.016} \quad (8)$$

Values of a, calculated from this equation, are included in Table 1. It will be noticed that they are small compared to the total amount of heat transferred to the calorimeter. A large relative error in a is not of much importance, therefore, for the accuracy of the final results.

The latent heat of vaporization constitutes a large part of the total heat content of the vapor. The sensible heat of the superheated steam, defined as $H_t - H_{100}$, is obtained separately, as may be seen from equation (3), by subtracting 11,069 cal.$_{15}$ mole^{-1} from the total heat content, $H_t - H_{25}$. Average values for the sensible heat, obtained by other methods, may be calculated directly by means of the formula[7] for the mean specific heat of superheated steam between 100° C. and t°C., and at a pressure of 1 atmosphere,

$$c_{100,t} = 0.4574 + 0.0000462t \quad (9)$$

In the range between 270° and 1,400° C. this formula is based upon the trustworthy experimental results of Holborn and Henning,[8] obtained by measuring the amount of heat given up to a calorimeter by a stream of superheated steam, not permitted to condense in the calorimeter. Observed and calculated values of the sensible heat, or, in other words, experimental values obtained in this investigation and values calculated from equation (9), are included in Table 1, together with the deviation between them in per cent. The agreement is quite satisfactory; in fact, the average numerical deviation is only 2.44 per cent.

The agreement between observed and calculated values of the sensible heat is further illustrated in Figure 3, in which the experimentally determined values given in Table 1 are shown together with a curve obtained by means of equation (9); that is to say, a curve based upon the experimental work of Holborn and Henning. It is concluded that although the method described is not to be considered as an improvement in regard to determinations of the heat content of superheated steam, it certainly can be applied to phosphorus pentoxide vapor with the expectation of obtaining results accurate within a few per cent.

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[7] Holborn, L., Scheel, K., and Henning, F., Wärmetabellen der physikalisch-technischen Reichsanstalt (Vieweg and Sohn, Braunschweig), p. 58, 1919.

[8] Holborn, L., and Henning, F., Ann. Physik, vol. 18, p. 739, 1905; vol. 23, p. 809, 1907.

4. RESULTS FOR PHOSPHORUS PENTOXIDE

Data obtained in 13 experiments performed on phosphorus pentoxide vapor are summarized in Table 2. The furnace temperatures were measured directly, as in the experiments with steam. As the vapor pressures of the amorphous and the vitreous modifications of phosphorus pentoxide are less than one atmosphere at temperatures below 600° C., condensation of the vapor into one of these modifications might be expected to take place below that temperature. However, no indication of such a condensation was observed; in fact, the vapor came through the furnace in the two first runs, with a furnace temperature of 549° C., as well as in all the other runs, overcoming the external pressure of one atmosphere; and afterwards no traces of solid phosphorus pentoxide were found in the silica tube. This indicates that the transformation requires higher pressures, such as are easily obtained in closed systems.

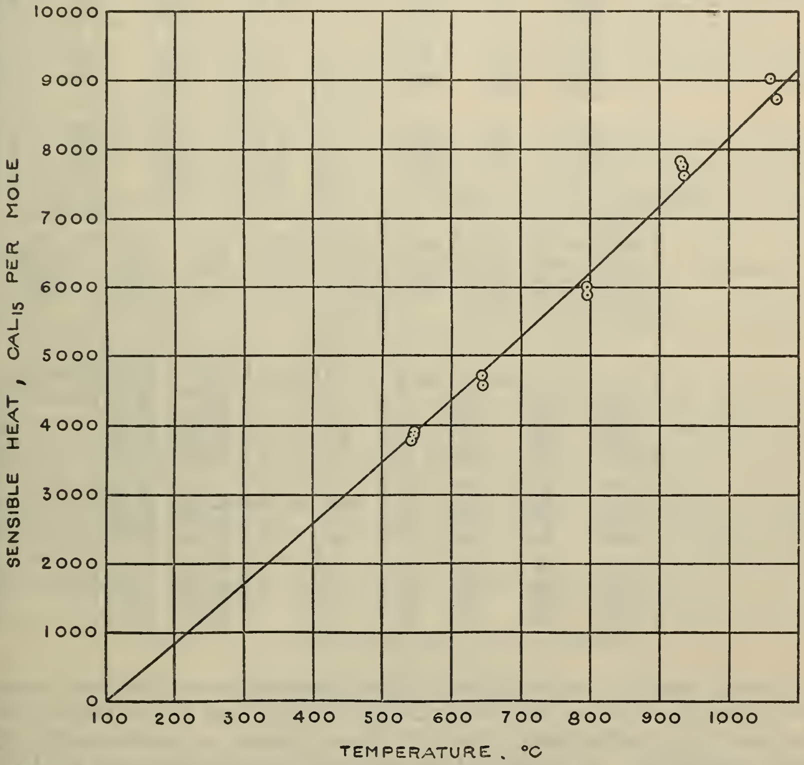

FIGURE 3.—*The sensible heat of steam at atmospheric pressure as a function of the temperature*

The curve is based upon data obtained by Holborn and Henning. ⊙, indicates results found with apparatus shown in Figure 1.

TABLE 2.—*Determinations of the heat content of phosphorus pentoxide vapor*

Run No.	Furnace temperature	Well-orifice drop	Temperature of vapor at orifice	Experimental period	Weight of phosphorus pentoxide	Equivalent rate of steam	Evaporated water	Final calorimeter temperature
	°*C.*	°*C.*	°*C.*	*Min.*	*g(vac.)*	*g min.*$^{-1}$	*g*	°*C.*
1	549	4	545	1.5	6.848	2.357	0.015	23.19
2	549	4	545	1.5	6.728	2.317	.040	23.08
3	655	5	650	2.0	11.011	2,790	.040	25.29
4	655	5	650	2.0	17.407	4.408	.296	26.69
5	812	8	804	1.5	9.105	2.996	.065	26.45
6	805	11	794	1.5	4.161	1.369	.033	24.35
7	801	9	792	1.5	7.203	2.372	.050	25.45
8	949	26	923	1.5	2.360	.758	.026	21.88
9	950	20	930	1.5	8.771	2.818	.080	24.50
10	958	22	936	1.5	9.594	3.079	.088	24.70
11	1,098	36	1,062	1.5	13.889	4.358	.100	26.63
12	1,098	37	1,061	1.5	12.159	3.813	.489	25.97
13	1,095	37	1,058	1.5	12.159	3.813	.036	25.81

Run No.	Total heat measured in calorimeter	Correction from blank experiments	Increase of radiation from spout	Heat lost from neck	Heat lost by evaporation of water	Correcting to 25° C. (add)	Heat of solution	Heat content of vapor H_t-H_{25}	$\frac{\text{Obs.}-\text{Calc.}}{\text{obs.}}\times 100$
	cal.$_{15}$	*cal.*$_{15}$	*cal.*$_{15}$	*cal.*$_{15}$	*cal.*$_{15}$	*cal.*$_{15}$	$\frac{cal._{15}}{mole^{-1}}$	$\frac{cal._{15}}{mole^{-1}}$	*Per cent*
1	3,710	254	3	76	9	−2	45,950	27,400	2.26
2	3,590	254	3	74	25	−2	45,910	26,490	−1.09
3	6,052	357	7	103	25	0	47,020	28,000	−9.47
4	9,358	256	7	103	182	5	48,220	28,350	−8.11
5	5,631	326	10	91	40	2	46,560	38,130	4.77
6	2,677	344	10	42	20	−1	45,110	36,300	.96
7	4,496	296	10	72	31	1	46,060	38,600	7.07
8	1,998	538	18	29	16	−1	44,460	44,990	9.55
9	5,766	506	18	109	49	−1	46,490	40,950	.00
10	6,261	494	18	119	54	−1	46,700	40,970	−.49
11	9,222	508	25	206	61	4	47,630	44,000	−4.11
12	8,015	520	25	206	301	2	47,280	45,930	.35
13	8,045	528	25	206	22	2	47,280	42,930	−6.36

In each run the temperature of the vapor at the orifice was calculated from the furnace temperature, the rate of flow of the vapor, and the observed temperature drop of steam under approximately the same conditions. In making this calculation it was assumed that the temperature drop of the phosphorus pentoxide vapor between the thermocouple well and the orifice was the same as that of steam at the same temperature, and flowing at an equivalent rate, defined by the relation

$$r_1c_1 = r_2c_2 \tag{10}$$

where r is the rate of flow, c is specific heat, and the subscripts 1 and 2 refer to phosphorus pentoxide and steam, respectively. The rate r_1, of a stream of phosphorus pentoxide is found by dividing the amount, w, condensed during the experiment by the experimental period, p. Values of w and p are given in Table 2. Values of c_2 are obtained from the literature;[9] and c_1 is constant and equal to 0.26 cal.$_{15}$ per g, as will be shown later. Equivalent rates of steam, calculated from equation (10), are included in Table 2. The temperature drop of the steam at the rate r_2, was calculated from the observed temperature drop at the same furnace temperature and at a rate of flow r_s by means of the equation

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[9] See footnote 7, p. 44.

$$d_2 = d_s \cdot \left(\frac{r_s}{r_2}\right)^{0.2} \tag{11}$$

where d represents temperature drop, and the subscripts refer to the two rates of flow.

Equation (11) is an approximate relation derived, after making certain simplifying assumptions, from an equation given by Walker, Lewis, and McAdams[10] for the heat lost by a fluid flowing through a tube of lower temperature. Equation (11) was tested for steam at a furnace temperature of about 600° C., and at rates ranging from 1.3 to 6.0 g per minute, and found to represent the measurements within the limits of their accuracy.

Corresponding values for the temperature drop of steam and the rate of flow, observed at different furnace temperatures, are given in Table 3. Substitution of these values, and the equivalent rates, in equation (11) gives values for the well-orifice drop in the phosphorus pentoxide experiments. In some runs, however, there is an additional correction, owing to the use of a preheating period shorter than the usual three minutes required to bring the spout to a constant maximum temperature. In such runs a small correction was added to the calculated drop in temperature.

For example, in run 6 the furnace temperature was 805° C. and the equivalent rate 1.369 g of steam per minute; Table 3 gives $d_s = 8°$C. and $r_s = 3.61$ g of steam per minute at 806° C.; substitution in equation (11) then gives $d_2 = 9.7°$ C. In this run the heating period was only 2.5 minutes, on account of which a correction of about 1.5° C. must be added, according to separate experiments with steam. The well-orifice drop in run 6 was, therefore, 11° C. Subtraction of this from the furnace temperature gives 794° C. for the temperature of the phosphorus pentoxide vapor at the orifice of the spout.

TABLE 3.—*Supplementary experiments with steam*

Furnace temperature	Rate of vaporization	Well-orifice drop
° C.	*g min*$^{-1}$	° C.
549	4.31	3
655	3.63	5
806	3.61	8
952	3.61	17.5
1,097	3.83	36

The amount of phosphorus pentoxide collected in the calorimeter was determined by gravimetric analysis, according to the method of Hoffman and Lundell.[11] Because a small amount of water evaporated from the calorimeter, the increase in weight of the calorimeter during the experimental period of a run was always a little less than the analytically determined weight of phosphorus pentoxide. The weight of evaporated water was easily determined by difference, and a correction was made for its heat of vaporization. The amount of heat lost from the neck of the Dewar flask was greater in runs 3 and 4 than in runs 1 and 2 on account of a longer experimental period, and less around 800° C. than at 550° and 650° C. on account of less condensation in the neck of the Dewar flask. Above 800° C. it increases with the temperature of the vapor.

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[10] Walker, H., Lewis, W. K., and McAdams, W. H., Principles of Chemical Engineering (McGraw-Hill Book Co., New York, N. Y.), pp. 135, 149, 1927.

[11] Hoffman, J. I., and Lundell, G. E. F., B. S. Jour. Research, vol. 5 (RP200), p. 279, 1930.

The heat content of the vapor at the orifice temperature is calculated from the equation

$$H_t - H_{25} = \left[Q - b - \Delta r + \Delta n + (t_f - 25) \cdot w \cdot s_{25} + \frac{e}{18.016} \times 11{,}069 \right] \frac{M}{w} - Q_{(soln.)} \tag{12}$$

in which the significance of Q, b, Δr, Δn, and t_f is the same as in the experiments with steam; H_{25} is the molal heat content of the crystalline phosphorus pentoxide at 25° C.; w designates the weight of phosphorus pentoxide collected in the calorimeter; e, the weight of water evaporated between the calorimetric fore and after periods; and M, the molecular weight, 142.04, of phosphorus pentoxide. The specific heat, s_{25}, of crystalline phosphorus pentoxide at 25° C. and the heat of solution, Q (soln.), of the same substance are obtained from equation (20) and Figure 8, respectively, both of which are given later.

In Figure 4 the experimentally determined values for the heat content of the vapor, calculated by means of equation (12), are shown plotted against the temperature. It is seen that the results are best represented by a straight line. From the molecular weight determinations of Tilden and Barnett [12] it is known that the molecular formula of phosphorus pentoxide vapor at bright red heat is more nearly P_4O_{10} than P_2O_5. The simpler formula and the name phosphorus pentoxide are employed merely for convenience. The equation for the straight line, calculated from the data in Table 2 by the method of least squares, is found to be

$$H_t - H_{25} = 6{,}720 + 36.81t \tag{13}$$

The deviations of the observed values from the curve average 4.20 per cent, as against 2.44 per cent in Table 1. The increase in error may probably be ascribed to irregularities in the heat of solution of phosphorus pentoxide, which, as shown later, depends upon the relative amounts of meta- and orthophosphoric acids formed in the solution.

The "error," m_o, of the straight line, computed as

$$m_o = 2\sqrt{\frac{m^2}{n(n-1)}} \tag{14}$$

where n is the total number of observations, and m represents deviations of the observed values from the straight line, is 1,170 calories per mole. Barring constant errors, this means that the probability that values for the heat content calculated from equation (13) differ from the true values of this quantity by more than 1,170 calories per mole, is only 4.55 per cent. However, the "error" of the heat of solution of crystalline phosphorus pentoxide, namely, ±560 calories per mole, is transferred to the preceding determinations of the heat content of the vapor. Hence the total "error" of the straight line is

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[12] Tilden, W. A., and Barnett, R. E., J. Chem. Soc., vol. 69, p. 154, 1896.

$$\pm\sqrt{1{,}170^2+560^2}=\pm 1{,}300 \text{ cal.}_{15} \text{ mole}^{-1}$$

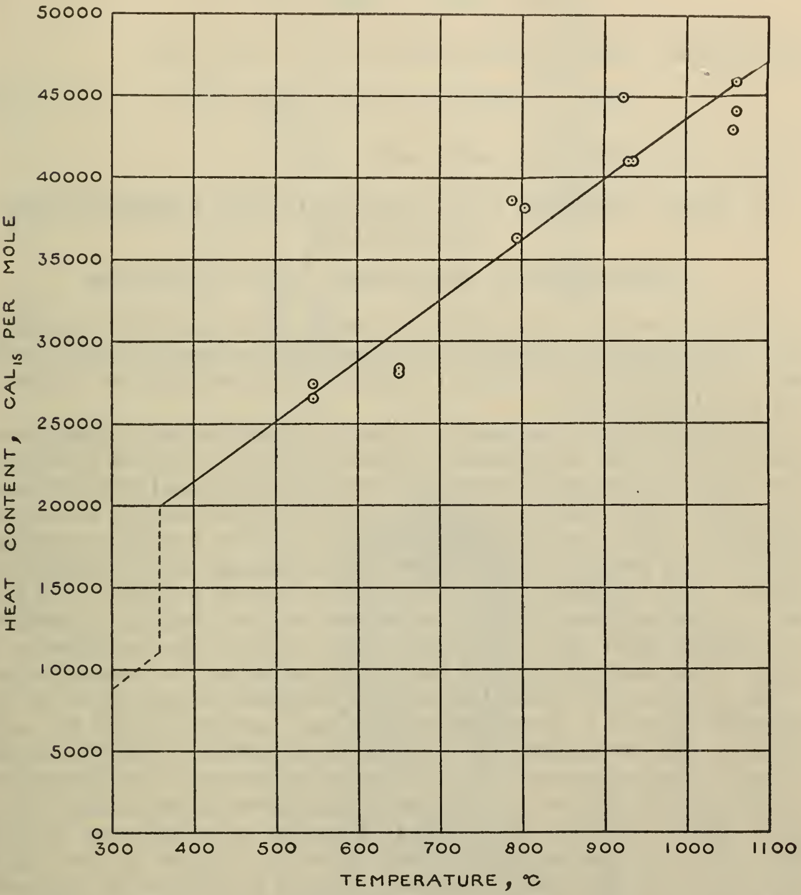

FIGURE 4.—*The heat content of phosphorus pentoxide vapor at atmospheric pressure as a function of the temperature*

The complete equation for the heat content of the vapor is then

$$H_t-H_{25}=(6{,}720+36.81t)\pm 1{,}300, \text{ cal.}_{15} \text{ mole}^{-1} \qquad (15)$$

The molal heat capacity, $C_{p,\,1\text{ atm.}}$, of the vapor equals the slope of the line in Figure 4, which is constant and equal to 36.81 calories per mole per degree. The error of the slope, δ, is not affected by the error of the heat of solution, but is determined solely by the accidental errors of the heat content determinations. Attributing two-thirds of the "error" calculated from these to the second term of the right side of equation (13), we have

$$\delta \times t = \pm \tfrac{2}{3} \times 1{,}170 \text{ cal.}_{15} \text{ mole}^{-1} \tag{16}$$

Substituting 800° C. for *t* as the approximate average of the experimental temperatures, we find

$$\delta = \pm 1.0 \text{ cal.}_{15} \text{ mole}^{-1}{}^{\circ}\text{C.}^{-1}$$

The molal heat capacity of the vapor is then found to be

$$C_{p,\ 1\ \text{atm.}} = 36.8 \pm 1.0, \text{ cal.}_{15} \text{ mole}^{-1}{}^{\circ}\text{C.}^{-1} \tag{17}$$

between the sublimation point and 1,100° C.

IV. HEAT CAPACITY OF CRYSTALLINE PHOSPHORUS PENTOXIDE

1. EXPERIMENTAL EQUIPMENT AND PROCEDURE

The heat content of samples of the usual metastable, crystalline form of phosphorus pentoxide was determined calorimetrically by the method of mixtures, in a manner similar to that described by Andrews, Lynn, and Johnston.[13]

The samples were prepared by vacuum sublimation of phosphorus pentoxide, purified as previously described, from a quartz flask into thin-walled quartz tubes about 10 mm in diameter and 165 mm long. The tubes were sealed off without breaking the vacuum, and a fine constantan wire was attached to each tube for transfer purposes. The vacuum permits sublimation at a relatively low temperature, whereby transformation into the vitreous form is avoided. To provide a means of determining the amount of heat lost in transferring the samples from the high-temperature bath to the calorimeter, a similar, evacuated quartz tube containing metallic silver was prepared.

The samples were heated to various constant temperatures in the range 25° to 212° C. in a narrow glass tube, covered at the top with asbestos, and surrounded by the saturated vapors of various liquids boiling at atmospheric pressure. The apparatus used for this purpose is illustrated in Figure 5. Higher temperatures were attained in a hollow brass cylinder, the internal diameter of which was slightly larger than the specimen tubes, and which was placed in the middle portion of a tubular electric furnace plugged at the bottom and covered at the top with asbestos. At the end of the heating period the brass body was lifted to the top of the furnace by means of a wire attached to it, and the sample immediately transferred to the calorimeter. In order to make sure that the samples each time would reach the temperature of the heating bath, they were always left in it for at least three hours. By separate determinations it was found that after this length of time none of the samples would take up a measurable amount of heat. Similarly, it was found that an after period of about one hour was necessary and sufficient to insure complete temperature equalization in the calorimeter.

The calorimeter consisted of a silvered Dewar tube, 5.1 by 25.4 cm, surrounded by appropriate insulating material, and containing about

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[13] Andrews, D. H., Lynn, G., and Johnston, J., J. Am. Chem. Soc., vol. 48, p. 1274, 1926.

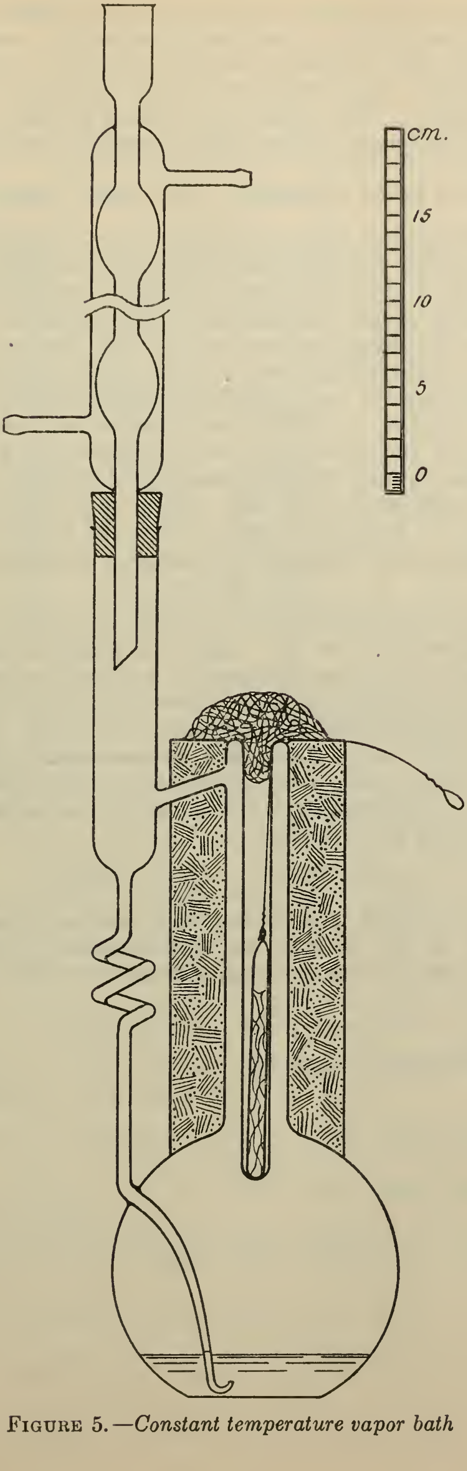

Figure 5.—*Constant temperature vapor bath*

300 g of water, a hand-operated stirrer, and a Beckmann thermometer. The calorimeter was kept in a room with practically constant temperature and only brought out during the few moments required for transferring the sample. Its heat capacity was accurately determined by electrical calibration. The true temperature rise in the calorimeter was determined by the graphic method described by Dickinson.[14]

2. DATA, HEAT CONTENT, AND HEAT CAPACITY

Experimental results obtained with three different samples of phosphorus pentoxide are given in Table 4. The weights in vacuum of the three tubes, and of their contents, were determined subsequent to the calorimetric measurements from the weight of the specimens before and after breaking and removal of the contents, respectively. The heat lost in transferring the samples from the high-temperature bath to the calorimeter was calculated from determinations made with the silver sample, in which the transfer loss was found as the difference between the calculated and the observed heat content of the sample. The amount of heat transferred with the silica containing-tubes was calculated from the range of cooling and the heat capacity of silica.[15] In order to refer the results to 25° C. as the lower end of the experimental temperature range, a correction

$$f=(t_f-25)\cdot w\cdot s_{25}$$

was added to the measured heat content; as before, t_f is the final calorimeter temperature, w the weight of phosphorus pentoxide in the sample, and s_{25} the specific heat of crystalline phosphorus pentoxide at 25° C., which later will be shown to be 0.17 calorie per gram. Above 250° C. vaporization of phosphorus pentoxide within the tube becomes appreciable and a correction, i, was made for this as shown in the table. The molal heat content of crystalline phosphorus pentoxide, H_t, at a temperature, t° C., less its heat content at 25° C., was calculated from the equation

$$H_t-H_{25}=[Q+q-Q_s+f-i]\times\frac{M}{w} \tag{18}$$

where Q is the amount of heat measured in the calorimeter, q the heat lost in transfer, Q_s the amount of heat transferred with the silica-containing tube, and M the molecular weight, 142.04, of phosphorus pentoxide.

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[14] See footnote 4, p. 40.

[15] International Critical Tables, vol. 5, p. 105, 1929.

TABLE 4.—*Determinations of the heat content of crystalline phosphorus pentoxide*

Run No.	Bath temperature	Weight of phosphorus pentoxide	Weight of silica	Final calorimeter temperature	Heat transferred to calorimeter	Heat lost in transfer	Heat transferred with silica	Correcting to 25° C. (add)	Correction for vaporization	Heat content of phosphorus pentoxide	$\frac{\text{Obs.}-\text{Calc.}}{\text{Obs.}}\times 100$
	° C.	*g (vac.)*	*g (vac.)*	*° C.*	*cal.₁₅*	*cal.₁₅*	*cal.₁₅*	*cal.₁₅*	*cal.₁₅*	*cal.₁₅ mole⁻¹*	*Per cent*
1	34.90	12.7209	7.0476	23.56	38.59	0.2	14.45	−3.11	--------	237	−0.8
2	76.57	12.7209	7.0476	22.67	189.62	1.4	70.55	−5.04	--------	1,289	−4.2
3	131.2	12.7209	7.0476	23.15	423.2	3.0	146.7	−4.00	--------	3,076	4.0
4	183.3	12.7209	7.0476	24.03	630.8	6.0	225.0	−2.10	--------	4,575	−1.0
5	238.0	12.7209	7.0476	24.63	889.4	9.4	312.7	−.80	--------	6,536	.1
6	36.0	8.8274	6.8536	24.25	32.7	.1	14.11	−1.26	--------	280	.7
7	64.4	8.8274	6.8536	25.48	112.1	.5	48.8	.72	--------	1,038	3.5
8	99.9	8.8274	6.8536	25.60	220.4	1.0	95.9	.90	--------	2,034	1.5
9	131.4	8.8274	6.8536	25.52	321.0	1.7	139.9	.78	--------	2,954	0
10	164.5	8.8274	6.8536	25.64	434.0	3.2	188.7	.96	--------	4,015	.1
11	183.6	8.8274	6.8536	26.42	500.8	3.8	216.9	2.13	--------	4,663	.8
12	210.2	8.8274	6.8536	26.93	595.4	5.0	257.3	2.90	--------	5,568	.4
13	76.57	3.2269	10.1655	22.84	131.1	1.4	101.45	−1.19	--------	1,314	−1.8
14	131.2	3.2269	10.1655	23.89	277.7	3.3	210.2	−.61	--------	3,089	4.5
15	183.3	3.2269	10.1655	24.98	416.2	6.4	322.5	−.01	--------	4,406	−5.0
16	239.0	3.2269	10.1655	24.09	590.4	10.4	453.8	−.50	--------	6,449	−1.8
17	288.0	3.2269	10.1655	24.69	758.5	15.7	570.9	−.17	0.29	8,928	6.3
18	288.0	3.2269	10.1655	25.04	752.4	15.7	570.0	.02	.29	8,708	3.9
19	335.0	3.2269	10.1655	24.23	886.6	22.2	690.1	−.42	1.49	9,543	−6.6
20	335.0	3.2269	10.1655	24.53	888.0	22.2	689.8	−.26	1.49	9,623	−5.7

Figure 6 shows the molal heat content in Table 4 plotted against the temperature, and a curve representing the graphic average of the experimental results. It is seen that the results obtained with the three different samples generally are in good agreement, in spite of the fact that the respective weights of phosphorus pentoxide and the relative amounts of silica in the samples were quite different. The deviations of the experimental results from the curve indicate the precision of the results, and are given in the last column of Table 4. The average deviation from the curve is 2.63 per cent, whereas the "error" of the curve itself is computed to be 1.57 per cent by means of equation (14).

The curve in Figure 6 is closely represented by the equation

$$H_t - H_{25} = (-578.2 + 22.17t + 0.03902t^2 - 2.817\times 10^{-5}\times t^3) \pm 1.57 \text{ per cent, cal.}_{15}\ \text{mole}^{-1} \qquad (19)$$

By differentiation of this equation the heat capacity of metastable, crystalline phosphorus pentoxide is found to be

$$C_p = \frac{dHt}{dt} = 22.17 + 0.07804t - 8.451\times 10^{-5}t^2, \text{ cal.}_{15}\ \text{mole}^{-1}\ {}^\circ C.^{-1} \qquad (20)$$

The "error" of values for C_p calculated from this expression is estimated to be 1.6 per cent.

According to equation (20) the heat capacity of crystalline phosphorus pentoxide increases with the temperature. We find, for example

$$C_{25} = 24.07 \pm 0.38, \text{ cal.}_{15}\ \text{mole}^{-1}\ {}^\circ C.^{-1}$$

and

$$C_{300} = 38.08 \pm 0.60, \text{ cal.}_{15}\ \text{mole}^{-1}\ {}^\circ C.^{-1}$$

The specific heat at 25° C. is

$$c_{25}=0.1694\pm0.0027,\ \text{cal.}_{15}\ g^{-1}\ {}^{\circ}C.^{-1}$$

It must be remembered that equations (19) and (20) have only been shown to apply in the range from 25° to about 350° C.

V. HEAT OF SUBLIMATION OF CRYSTALLINE PHOSPHORUS PENTOXIDE

The sublimation point of metastable, crystalline phosphorus pentoxide, is found from plots of various vapor pressure determinations against the temperature, as the temperature at which the vapor pressure is equal to one atmosphere. The determinations by Hoeflake and Scheffer[16] give 359.0° C. as the sublimation point. Three sets of determinations by Smits and Deinum[17] lead to the values 356.6°, 362.0°, and 370.5° C., respectively; the average of these three temperatures is 363.0° C. Two sets of determinations by Smits and Rutgers[18] give 354.9° and 346.1° C., respectively, or an average value of 350.5° C. The mean of these three average values, finally, gives 358±7° C. as the sublimation point. At this temperature the heat content of the vapor is

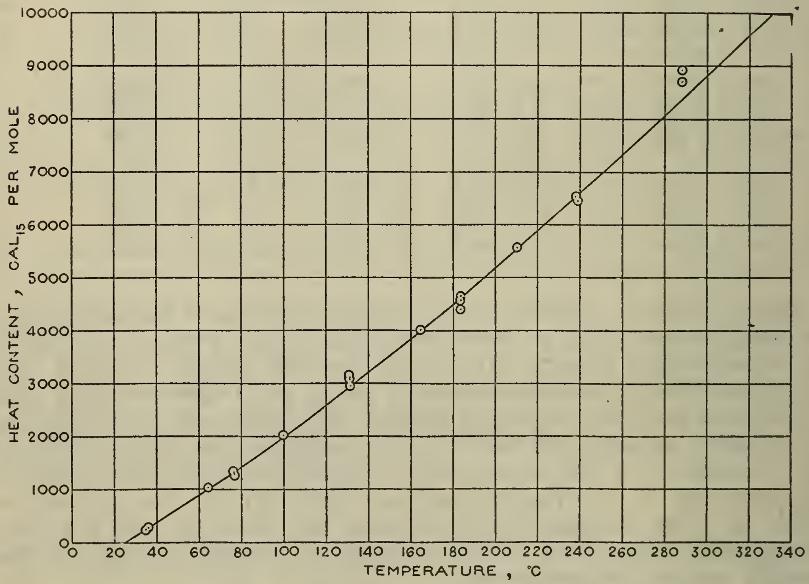

FIGURE 6.—*The heat content of the ordinary crystalline form of phosphorus pentoxide as a function of the temperature*

$$H_{358}^{(vap.)}-H_{25}^{(cryst.)}=19{,}900\pm1{,}300,\ \text{cal.}_{15}\ \text{mole}^{-1}$$

according to equation (15); and the heat content of the solid is

$$H_{358}^{(cryst.)}-H_{25}^{(cryst.)}=11{,}070\pm170,\ \text{cal.}_{15}\ \text{mole}^{-1}$$

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[16] Hoeflake, J. M., and Scheffer, M. F., Rec. trav. chim., vol. 45, p. 191, 1926.
[17] Smits, A., Z. physik. Chem., Abt. A, vol. 149, p. 337, 1930.
[18] Smits, A., and Rutgers, A. J., J. Chem. Soc., vol. 125, p. 2573, 1924.

according to equation (19). The heat of sublimation, found as the difference between the heat content of the vapor and of the solid, respectively, is then

$$L_{(subl.)} = 8{,}800 \pm 1{,}300, \text{ cal.}_{15} \text{ mole}^{-1} \qquad (21)$$

In Figure 4 the heat of sublimation is represented graphically by the sudden increase in heat content of phosphorus pentoxide at the sublimation point.

VI. HEAT OF SOLUTION OF CRYSTALLINE PHOSPHORUS PENTOXIDE

Several samples of crystalline phosphorus pentoxide were prepared by subliming purified phosphorus pentoxide from a half-liter glass flask into a glass tube with several constrictions, sealed to the flask at one end and connected to a P_2O_5 drying tube, open to the atmosphere, at the other. The sublimation was carried out at atmospheric pressure, under which conditions formation of the vitreous modification of phosphorus pentoxide in the sublimed product does not occur. After sublimation the glass tube was sealed off at the constrictions, and the samples were weighed.

The heat of solution was determined in a large silvered Dewar flask containing about 1,500 g of distilled water at room temperature, and a Beckmann thermometer. As usual the heat capacity of the calorimeter was determined by electrical calibration. The sample tube was placed in the water and allowed to remain until complete temperature equalization had taken place, when it was broken under the water with a long, specially made screw clamp of the same temperature as the water. To avoid transfer of heat from the hands of the operator through the screw clamp to the water, the screw clamp was covered at the upper end with rubber and at the lower end with vaseline. The weight of the glass from the broken sample was carefully determined after the calorimetric experiment, and the weight of phosphorus pentoxide was then found by difference.

The results of five determinations are given in Table 5. It is noticed that the weights of phosphorus pentoxide, and therefore also the concentrations of the resulting solutions, cover the same range as those in Table 2. Furthermore, the final calorimeter temperatures are nearly identical in the two tables. The heat of solution may, therefore, be expected to be practically the same in these two series of experiments. To the heat capacity of the calorimeter must be added that of the sample and containing tube. A deduction is made for the small amount of mechanical energy added to the system by breaking the sample-containing tube. A series of preliminary experiments showed that in the concentration range considered here the heat of solution decreases with decreasing concentration in spite of the heat of dilution of phosphoric acid. In order to find out whether this is caused by a variation in the relative amounts of meta-and orthophosphoric acids formed, the solution in each experiment given in Table 5 was titrated immediately after the calorimetric measurements, first with methyl orange indicator, to which the first hydrogen ion of both acids is acid, and second with phenolphthalein, to which the second hydrogen ion of orthophosphoric acid is acid,[19] and from the results was calculated the mole fraction of metaphosphoric acid in the mixture of meta-and orthophosphoric acids. The plot in

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[19] Prideaux, E. B. R., Chem. News, vol. 99, p. 161, 1909.

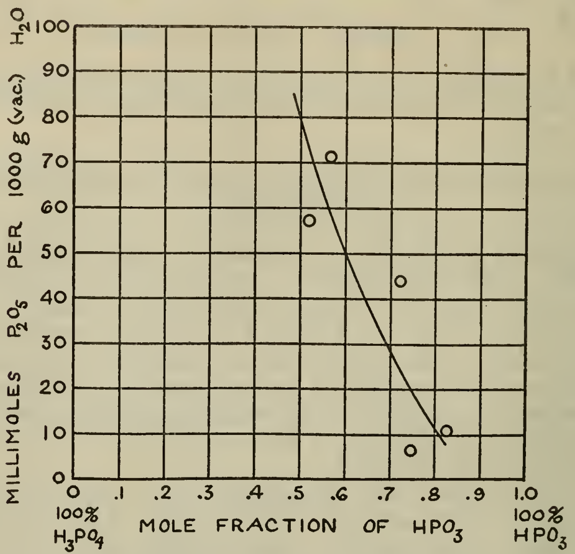

Figure 7.—*Variation, with the concentration, of the relative amounts of meta-and orthophosphoric acid, formed by solution of crystalline phosphorus pentoxide in water at 25° C.*

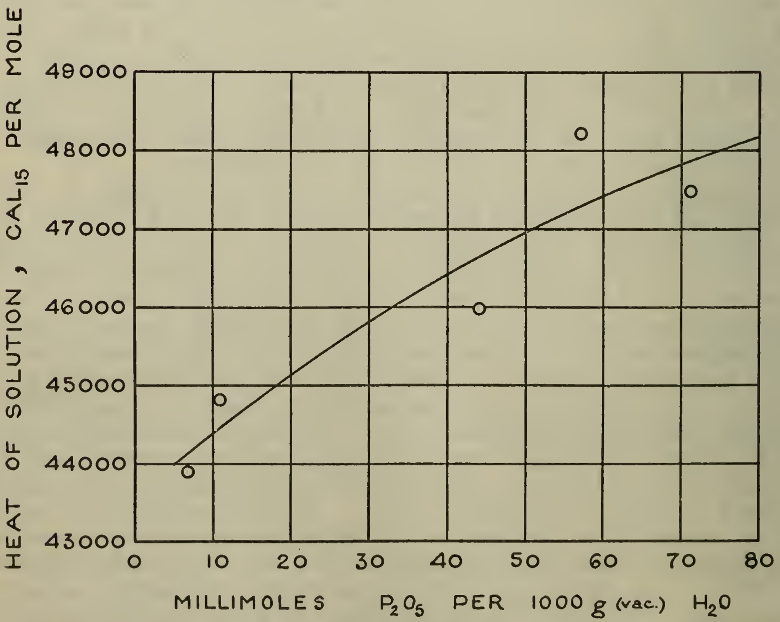

Figure 8.—*Heat of solution of the ordinary crystalline form of phosphorus pentoxide as a function of the concentration*

Figure 7 shows that the relative amount of metaphosphoric acid decreases with increasing concentration. As heat is evolved by the transformation of meta-into orthophosphoric acid, the observed increase in the heat of solution with increasing concentration is thereby explained. Figure 8 shows the heat of solution plotted against the concentration. The "error" of the curve, calculated from the deviations of the experimental results by means of equation (14), is found to be ± 560 calories.

TABLE 5.—*Determinations of the heat of solution of phosphorus pentoxide*

Run No.	Weight of phosphorus pentoxide	Millimoles P_2O_5 per 1,000 g (vac.) H_2O	Final calorimeter temperature	Heat evolved in calorimeter	Mole fraction of HPO_3	Heat of solution	$\frac{\text{Obs.-Calc.}}{\text{Obs.}} \times 100$
	g (vac.)		*° C.*	*cal.₁₅*		*cal.₁₅ mole₋₁*	*Per cent*
1	1.4351	6.74	26.4	443.5	0.748	43,890	−0.55
2	2.3318	10.94	26.4	735.8	.823	44,820	.80
3	9.3891	43.98	27.5	3,040.2	.722	45,990	−1.41
4	12.2138	57.10	28.2	4,145.8	.519	48,210	1.89
5	15.1624	71.18	29.0	5,068.1	.567	47,480	−0.80

The heat of transformation of meta- into orthophosphoric acid may now be calculated. Figure 7 shows that at a concentration of 11.5 millimoles of P_2O_5 per 1,000 g of H_2O, the mole fractions of HPO_3 and H_3PO_4 are 0.8 and 0.2, respectively. At this concentration the reaction attending the solution of one mole of phosphorus pentoxide is, therefore

$$P_2O_{5(cryst.)} + 1.4\ H_2O(l) + aq = 1.6\ HPO_{3(aq)} + 0.4\ H_3PO_{4(aq)} + (44{,}500 \pm 800)\ \text{cal.}_{15} \tag{22}$$

where the heat of solution has been obtained from Figure 8, and the "error" of both curves is included.

Similarly at 79.5 millimoles of P_2O_5 per 1,000 g H_2O the mole fractions of HPO_3 and H_3PO_4 are 0.5 each. The solution reaction is then

$$P_2O_{5(cryst.)} + 2\ H_2O(l) + aq = HPO_{3(aq)} + H_3PO_{4(aq)} + (48{,}200 \pm 800)\ \text{cal.}_{15} \tag{23}$$

In the concentration range considered here the heat of dilution of phosphoric acid[20] is negligibly small. Subtracting equation (22) from equation (23), and dividing both sides by 0.6, we find

$$HPO_{3(aq)} + H_2O(l) = H_3PO_{4(aq)} + (6{,}200 \pm 1{,}900)\ \text{cal.}_{15} \tag{24}$$

According to measurements by Giran[21] the amount of heat evolved in the last reaction is 3,150 calories. However, in dissolving pure metaphosphoric acid he made no correction for its partial conversion into orthophosphoric acid. Assuming that he obtained a conversion similar to that shown in Figure 7, his result becomes about 5,500 calories instead.

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[20] International Critical Tables, vol. 5, p. 180, 1929.

[21] Giran, H., Ann. chim. phys., vol. 30, p. 203, 1903.

From equations (23) and (24) one obtains by addition and subtraction, respectively

$$P_2O_{5(cryst.)} + 3\ H_2O(l) + aq = 2\ H_3PO_{4(aq)} + (54{,}400 \pm 2{,}100)\ \text{cal.}_{15} \qquad (25)$$

and

$$P_2O_{5(cryst.)} + H_2O(l) + aq = 2\ HPO_{3(aq)} + (42{,}000 \pm 2{,}100)\ \text{cal.}_{15} \qquad (26)$$

Hence it is seen that the heat of solution of phosphorus pentoxide in water at 25° C. may vary between 54,400 and 42,000 calories per mole of phosphorus pentoxide, according to the relative amounts of ortho- and meta-phosphoric acids formed in the solution. The values obtained by Giran [22] and Thomsen [23] are 40,790 and 35,600 calories per mole, respectively. It is thought that the samples of phosphorus pentoxide used by these investigators gave low results on account of possible contamination with lower oxides of phosphorus and metaphosphoric acid.

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[22] See footnote 21, p. 57.

[23] Thomsen, J., Thermochemistry (Longmans, Green & Co., New York), 1908.